Amorphous $AlPO_4$ as Catalyst Support. I. FTIR Study of CO Adsorbed on Chromocene and Trimethylsilylchromocene Reacted with $AlPO_4$

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After adsorption of CO on chromocene and trimethylsilylchromocene reacted with amorphous $AlPO_4$ the two CO IR bands at high wavenumbers are shifted by some 16 cm^{-1} to higher wavenumbers compared to previous studies using silica gel as a support. These bands are now at 2061/1990 and 2056/1980 cm^{-1}, respectively. CO IR bands shifted to lower wavenumbers are not observed. It is therefore concluded that chromocene reacts only with the more acidic phosphorus surface hydroxyl groups and not with the aluminium ones of the amorphous $AlPO_4$. It is also concluded that the electron density at the chromium atom is less on $AlPO_4$ compared to silica gel. The two CO IR bands are converted to three CO IR bands at lower wavenumbers (1923, 1832 and 1620 cm^{-1}) after several hours. For trimethylsilylchromocene this reaction was faster than for the unsubstituted chromocene.

The Union Carbide catalyst[1] is one of the three industrially important catalysts for the polymerization of ethylene. The catalyst consists of chromocene and silica gel. It is well known that chromocene reacts with one surface silanol group by forming a cyclopentadiene molecule and a cyclopentadienylchromium surface oxide.[1] Several modified chromocenes like bisindenyl- and bisfluoro-chromium have also been investigated as components in the polymerization catalyst.[2]

One of the present authors has studied the Union Carbide catalyst with CO IR spectroscopy.[3] It was found that five main CO IR bands can be observed: 2046, 1974, 1920, 1825 and 1620 cm^{-1}. After several hours the first two bands decrease in intensity and the three bands at lower wavenumbers increase. This is an indication that one chromium surface species with CO IR bands at 2046 and 1974 cm^{-1} is converted into another with the three CO IR bands at lower wavenumbers. Comparing this behaviour of the adsorption of CO with a similar one[3–5] observed with the Phillips catalyst[6] (another of the three catalysts used for the polymerization of ethylene), the above-mentioned conversion of CO IR bands was interpreted as a conversion of terminally bonded CO ligands into bridging ones. Another interpretation has been published recently in which the three CO IR bands at lower wavenumbers were assigned to a $(CpCr(CO)_3)^-$ species.[7]

Recent investigation of the reaction between substituted chromocenes and silica gel[8] showed that the position of the two CO IR bands at higher wavenumbers can be shifted to lower wavenumbers, but only to a relatively small amount (less than 10 cm^{-1}). Amorphous aluminium phosphates $(AlPO_4)$[9,10] have been known for a long time and have recently been used as a catalyst support for the Phillips and Union Carbide catalysts.[11–13] The aim of the present investigation is to use the CO IR technique in order to study the reaction of chromocenes with amorphous $AlPO_4$.

Experimental

Amorphous $AlPO_4$ was prepared from $x\mathrm{Al(NO_3)_3 \cdot 6H_2O}$ and $y\mathrm{(NH_4)_2HPO_4}$ [$x = 1$ (**1** and **2**), $y = 1.1(\mathbf{1}), 0.9(\mathbf{2})$]. An aqueous solution of these two substances was acidified with HNO_3 and then a gel formed by addition of a 25 % ammonia solution, so that the liquid became slightly alkaline.[14] The specific surface of the amorphous $AlPO_4$ was 140 $m^2\,g^{-1}$ and the pore volume was 0.3 $cm^3\,g^{-1}$. Chromocene[1] and trimethylsilylchromocene[15] were prepared as described in the literature.

65 mg of the $AlPO_4$ were pressed into a disc with a diameter of 2 cm and placed in an IR cell.[16] The cell was evacuated at 600 °C and cooled to room temperature (first IR spectrum). A toluene solution of the chromocene was then splashed on the disc with exclusion of air and the IR cell was evacuated again at room temperature. After recording the second spectrum the IR cell was filled with 80 Torr CO and more spectra were recorded after several hours. The spectra in Figs. 1–4 were calculated by subtracting the second spectrum from the CO spectra. In Fig. 5 the first and the second spectrum are used. The FTIR spectra were recorded with a Nicolet 20 SXC spectrometer. The resolution was 2 cm^{-1} and 1024 scans were averaged.

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Results

Fig. 1 shows the CO IR spectra of $AlPO_4$ (support **1**) discs after reaction with chromocenes. The chromocene catalyst shows two CO IR bands at 2061 and 1990 cm^{-1} and the trimethylsilylchromocene CO IR bands at 2056 and 1980 cm^{-1}. For both samples the CO IR bands are shifted to higher wavenumbers by some 10–20 cm^{-1}, when compared with bands observed with silica gel as the catalyst support (2047/1972 and 2041/1966 cm^{-1}, respectively).[8] Using an $AlPO_4$ sample with a different P/Al ratio (support **2**) only a small change in the CO IR spectra to 2061 and 1992 cm^{-1} was observed using unsubstituted chromocene (Fig. 2). Trimethylsilylchromocene gave essentially no difference between the two $AlPO_4$ supports. The width at half maximum of the two CO IR bands at higher wavenumbers was the same if either $AlPO_4$ or silica gel was used as the catalyst support.

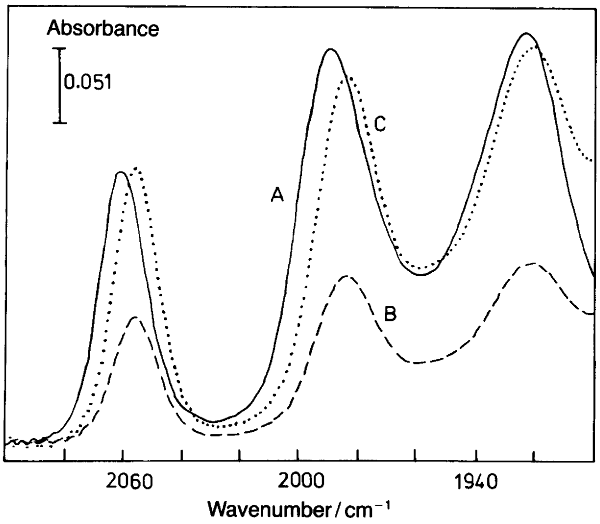

Fig. 1. CO FTIR spectra of amorphous $AlPO_4$ (support **1**) reacted with chromocene (A) and trimethylsilylchromocene (B). To ease the comparison between the two spectra, spectrum B was multiplied to the same height (C).

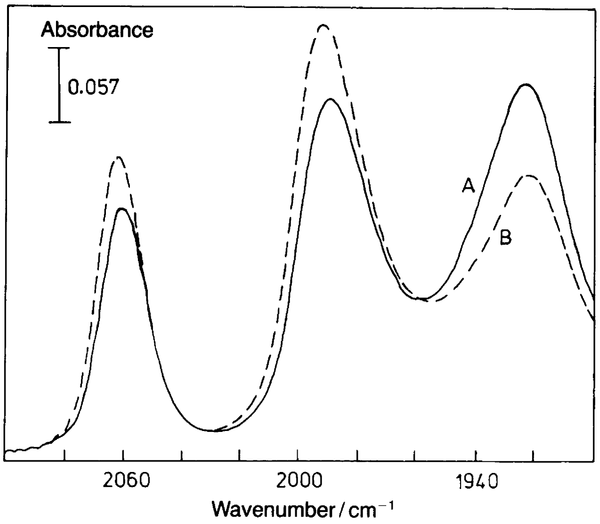

Fig. 2. CO FTIR spectra of chromocene reacted with different amorphous $AlPO_4$ supports. For spectrum A support **1** (P/Al: 1.1) and for spectrum B support **2** (P/Al: 0.9) was used.

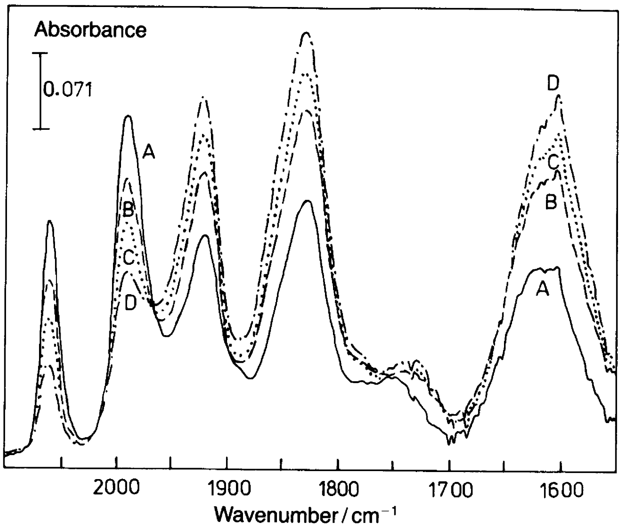

Fig. 3. CO FTIR spectra of chromocene/$AlPO_4$ (support **2**). Spectrum A is the initial spectrum and the spectra B, C and D were recorded after 1, 4 and 18 h, respectively.

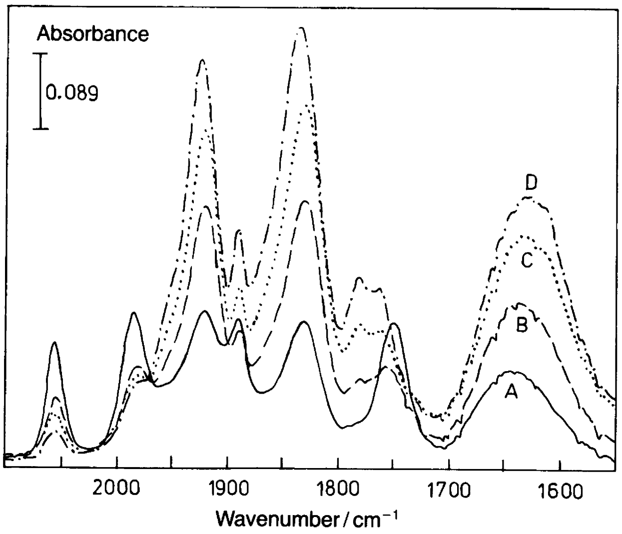

Fig. 4. As Fig. 3, but trimethylsilylchromocene was used as the chromium component of the Union Carbide catalyst instead of chromocene.

As mentioned above, three main CO IR bands at lower wavenumbers can be observed on chromocene/silica gel catalysts[3] at 1920, 1825 and 1620 cm^{-1}. As shown in Fig. 3, these three CO bands are also observed with chromocene/$AlPO_4$ (support **2**) catalysts at 1923, 1832 and 1616 cm^{-1}. The two CO IR bands at 2062 and 1992 cm^{-1} decrease, as has been observed previously, and the three CO bands at lower wavenumbers increase with time. One should notice that, while the two CO IR bands at higher wavenumbers

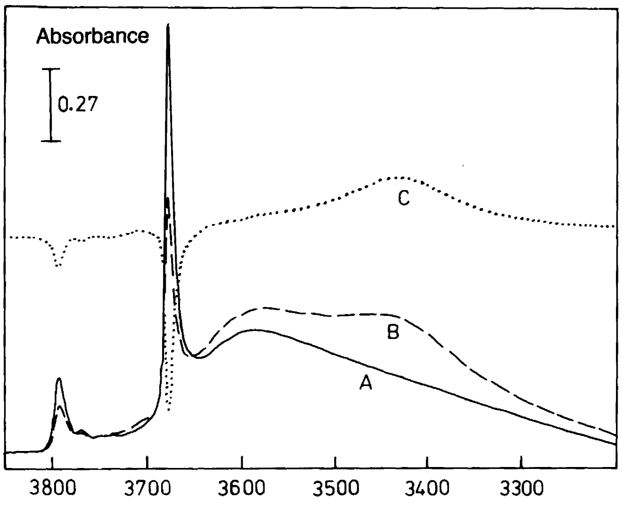

Fig. 5. FTIR spectra of the OH stretching region. Spectrum A is for the AlPO$_4$ evacuated at 600 °C (support **2**) and spectrum B after reaction with chromocene. Spectrum C is the difference of spectrum B minus spectrum A.

are shifted, the three CO IR bands at lower wavenumbers are essentially at the same position as for the chromocene/silica gel catalyst. A weak band at 1747/1732 cm^{-1} is also observed in Fig. 3.

Using the trimethylsilylchromocene as the chromium component of the Union Carbide catalyst (Fig. 4) one observes a faster conversion of the two CO IR bands at higher wavenumbers and the appearance of two additional low wavenumber bands at 1885 and 1743 cm^{-1}. The latter two bands decrease somewhat after 1 h, while the three bands at 1919, 1828 and 1624 cm^{-1} grow continuously with time. The two bands shift to 1886 and 1756/1776 cm^{-1} after some time and increase again in intensity.

It is well known that amorphous aluminium phosphates have different surface hydroxyl groups.[10] Fig. 5 A shows IR bands from stretching vibrations of surface aluminium hydroxyls at 3793 and 3768 cm^{-1} and of surface phosphorus hydroxyls at 3676 cm^{-1}. A very broad band at 3580 cm^{-1} is due to surface hydroxyl groups, most likely phosphorus ones, perturbed by a hydrogen bridge bond from a second surface hydroxyl band. This OH IR band vanishes almost completely on heating the sample in vacuum to 800 °C.

On reaction with chromocene the IR band at 3792 cm^{-1} from surface Al–O–H groups decreased by 39 % and the one at 3676 cm^{-1} from surface P–O–H groups by 49 % (Fig. 5 B). A new, very broad band at 3443 cm^{-1} also appears. The latter O–H IR band is most likely due to weak binding of the cyclopentadienyl ligand from the chromium cyclopentadienyl surface oxide to the surface hydroxyl groups. The decrease in the intensity of the surface OH groups on reaction with chromocene is mainly caused by this effect, but the difference for the surface AlOH and POH can not be explained in this way. This effect becomes more clear in the difference spectrum C in Fig. 5.

Discussion

Fig. 6 shows the separation of the two high-wavenumber CO IR bands from CO adsorbed on chromocenes reacted with amorphous supports versus the arithmetic mean of these two bands. In comparison with silica gel these bands are shifted by 16 or 17 cm^{-1} for amorphous aluminium phosphates (points A and B as compared to C and D in Fig. 6). This means that the oxygen ligand at the chromium surface ion is decreasing the electron density at the chromium atom and that this oxygen binds to a phosphorus ion of the support, because the phosphorus atom is clearly more electronegative than the aluminium atom (2.2 versus 1.6, calculated according to Pauling).[17]

One should bear in mind that silicon has an electronegativity of 1.9, just between those of Al and P. The stretching vibrations of surface hydroxyl groups follow the same trend; AlO–H, 3793; SiO–H, 3745; PO–H, 3676 cm^{-1}. If the surface aluminium hydroxyl groups of the amorphous aluminium phosphates were to react with chromocene, one would expect CO IR bands of CO adsorbed on the chromium shifted some 15 cm^{-1} to lower wavenumbers (CO IR bands at about 2030 and 1957 cm^{-1}) from those observed on chromocene/silica gel. However, such CO IR bands are not observed. The acidity of the Al–O–H groups seems to be insufficient to let them react with chromocene. The conclusion that chromocene only reacts with the P–O–H groups of the AlPO$_4$ is also supported by the slight difference in the decrease of the hydroxyl IR bands (AlOH, 39 %; POH, 49 %).

Polymerization measurements[13] of chromocene/AlPO$_4$ catalysts showed that, as for chromocene/silica gel cata-

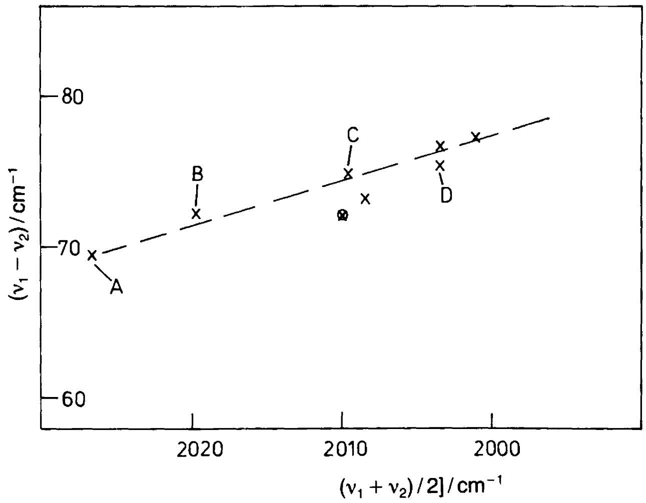

Fig. 6. Splitting of the two CO FTIR bands at higher wavenumbers from chromocene/support catalysts versus the arithmetic mean of these CO IR bands. The points A and B are from chromocene (A) and trimethylsilylchromocene (B) on AlPO$_4$ (support **2**) and the points C and D are from the same chromocenes on silica gel (Ref. 8). Other points are from differently substituted chromocenes on silica gel (Ref. 8).

lysts, the chain transfer is promoted by hydrogen addition to the catalytic site, and the molecular weight of the polymer is influenced strongly by the partial pressure of hydrogen. The molecular weight distribution of the ethylene polymer is narrow.[13] This catalytic behaviour can be explained by our results that chromocene only reacts with phosphorus surface hydroxyl groups.

For an open-ring chromocene (bis-dimethylpentadienylchromocene), however, a bimodal polymer weight distribution with two peaks was observed.[13] The peak for low molecular weight polymer was ascribed to catalytic surface sites linked to phosphorus atoms and the peak for high molecular weight polymer to arise from aluminium surface sites.[13] Catalysts formed by reaction of mixed open-ring, closed-ring chromocene with $AlPO_4$ showed that the open-ring ligand reacts more easily.[13] The open-ring chromocene might therefore also react with surface aluminium hydroxyl groups. This would explain the bimodal polymer weight distribution, where, however, the assignment of catalytic sites[13,18] should be inversed. A comparison of the polymer weight distributions for open-ring and closed-ring chromocene/$AlPO_4$ catalysts shows that the closed-ring catalyst produces high molecular weight polymers and second, as shown above by the CO FTIR spectra, the reaction between chromocene and the phosphorus hydroxyl groups decreases the electron density at the chromium. Less electron density at the chromium means that the catalytic site is less sensitive to hydrogen as a chain transfer agent. Therefore chromocene should form catalytic sites after reaction with POH surface groups, which would produce high molecular weight polymers, while after reaction with AlOH surface groups the catalytic sites should produce low molecular weight polymers.

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